UNCLASSIFIED

AD NUMBER

AD118822

CLASSIFICATION CHANGES

TO: unclassified

FROM: confidential

LIMITATION CHANGES

TO:

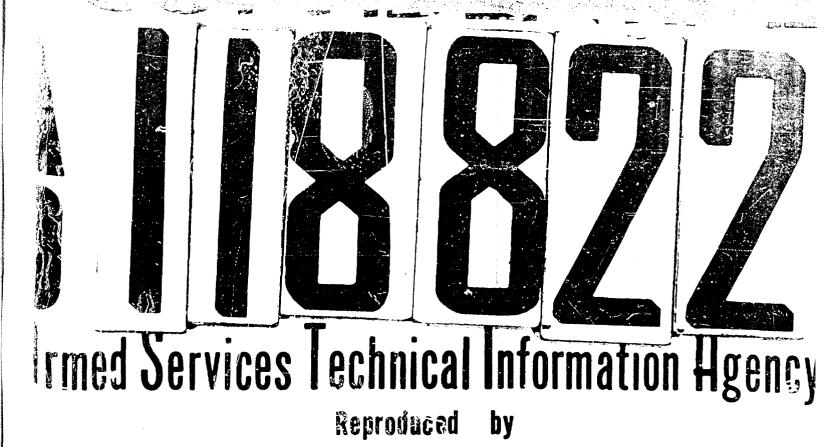
Approved for public release, distribution unlimited

FROM:

Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 01 NOV 1956. Other requests shall be referred to Naval Ordnance Systems Command, Washington, DC.

AUTHORITY

30 Nov 1968, DoDD 5200.10; USNSWC ltr, 4 Dec 1974



DOCUMENT SERVICE CENTER KNOTTBUILDING, DAYTON, 2, OHIO

This document is the property of the United States Government. It is furnished for the duration of the contract and shall be returned when no longer required, or upon recall by ASTIA to the following address: Armed Services Technical Information Agency, Document Service Center, Knott Building, Dayton 2, Ohio.

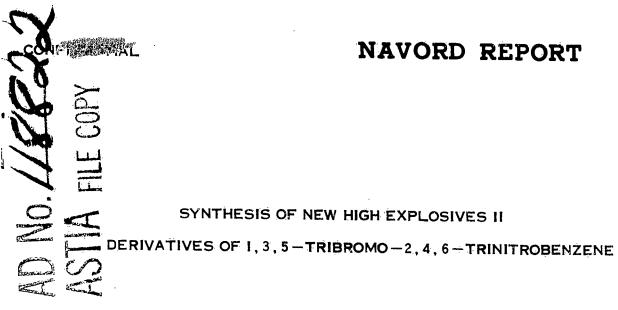
Jost Available Copy

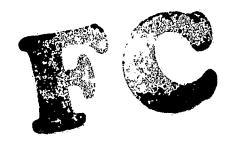
OTICE: WHEN GOVERNMENT OR OTHER DRAWINGS, SPECIFICATIONS OR OTHER DATA RE USED FOR ANY PURPOSE OTHER THAN IN CONNECTION WITH A DEFINITELY RELATED OVERNMENT PROCUREMENT OPERATION, THE U.S. GOVERNMENT THEREBY INCURS OF RESPONSIBILITY, NOR ANY OBLIGATION WHATSOEVER; AND THE FACT THAT THE OVERNMENT MAY HAVE FORMULATED, FURNISHED, OR IN ANY WAY SUPPLIED THE DRAWINGS, SPECIFICATIONS, OR OTHER DATA IS NOT TO BE REGARDED BY APLICATION OR OTHERWISE AS IN ANY MANNER LICENSING THE HOLDER OR ANY OTHER PROOF OR CORPORATION, OR CONVEYING ANY RIGHTS OR PERMISSION TO MANUFACTURE, OR SELL ANY PATENTED INVENTION THAT MAY IN ANY WAY BE RELATED THERETO.



NOTICE: THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C., SECTIONS 793 and 794.

THE TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROFIBITED BY LAW.





I NOVEMBER 1956



U. S. NAVAL ORDNANCE LABORATORY WHITE OAK, MARYLAND

JAN 18 1957

57AA 4759

"This publication is CONFIDENTIAL and shall be safe-guarded in accordance with the security provisions of the U.S. Navy Regulations and the provisions of applicable Federal Statutes and Executive Orders for Safe-guarding Classified Information. As stated in Article 0906.2 of OPNAVINST 5510.1A, dated 2 October 1954, it is forbidden to make extracts from or to copy this classified document without authorization."

NAVORD Report 4405

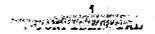
SYNTHESIS OF NEW HIGH EXPLOSIVES II, DERIVATIVES OF 1,3,5-TRIBROMO-2,4,6-TRINITROBENZENE

Prepared by FRANCIS TAYLOR, JR.

Approved by: DARRELL V. SICKMAN Chief, Chemistry Division

ABSTRACT: In the course of the investigation of the reactions of 1,3,5-tribromo-2,4,6-trinitrobenzene in the search for new high explosives, the preparation and physical properties of 1,3,5-triamino-2,4,6-trinitrobenzene, 1,3,5-tris methylamino-2,4,6-trinitrobenzene, and 1,3,5-tris methylamino-2,4,6-trinitrobenzene were studied. The triamino compound was found to be the most stable organic high explosive at elevated temperatures known to the author. It is much superfor to our present service explosives, and also possesses a higher crystal density, insensitivity to impact, and a higher detonation velocity than TNT. The tris methylamino and tris methyl-nitramino derivatives are new to the literature, but offer no advantage over present service explosives. Unsuccessful attempts were made to replace the bromine atoms of the starting material with other explosive contributing groups.

EXPLOSIVES RESEARCH DEPARTMENT U. S. NAVAL ORDNANCE LABORATORY White Oak, Silver Spring, Maryland



5711 4759

NAVORD Report 1405

1 November 1956

This report is a description of the preparation of derivatives of 1,3,5-tribromo-2,4,6-trinitrobenzene performed under Task NO 800-667/76004/01040. The reliability of the work and the validity of the conclusions are the responsibility of the author and of the Chemistry Division, Explosives Research Department, of the U. S. Naval Ordnance Laboratory. This report is for information only.

W. W. WILBOURNE Captain, USN Commander

J. E. ABLARD By direction

TABLE OF CONTENTS

	Page	No.
INTRODUCTION	. 1	
EXPERIMENTAL	. 2	
Preparation of 1,3,5-triamino-2,4,6-trinitrobenzene (TATNB)	• 2	
Preparation of 1,3,5-tris Methylamino-2,4,6-trinitro benzene		
Preparation of 1,3,5-tris Methylnitramino-2,4,6-trinitrobenzene	• 3	
Attempted preparation of 1,3,5-tricyano-2,4,6-trinitrobenzene	• 3	
Attempted preparation of 1,3,5-tris-5-aminotetrazole 2,4,6-trinitrobenzene		
Attempted reaction of 1,3,5-tribromo-2,4,6-trinitro- benzene with glycine ethyl ester hydrochloride	• 4	
Attempted preparation of 1,3,5-trihydroazine-2,4,6-trinitrobenzene	. 4	
Attempted preparation of 1,3,5-tris aminoguanidine- 2,4,6-trinitrobenzene		
Attempted preparation of 1,3,5-(2,2-dinitropropy1)-2,4,6-trinitrobenzene		
TABLE I Physical Properties	• 6	
TABLE II Detonation Velocities of 1,3,5-Triamino-2,4,6-Trinitrobenzene	• 7	
CONCLUSIONS	. 8	
ACKNOWLEDGEMENTS	. 8	
LIST OF REFERENCES	• 9	ř

SYNTHESIS OF NEW HIGH EXPLOSIVES II,
DERIVATIVES OF 1,3,5-TRIBROMO-2,4,6-TRINITROBENZENE

INTRODUCTION

This is the second of a series of reports on synthesis of new high explosives. The first of the series were "Preparation and Properties of 2',2',2'-Trinitroethyl-2,4,6-Trinitrobenzoate, Bis(2,2,2-Trinitroethyl)-Alpha Trinitroethyl Succinate, and Bis(2,2,2-Dinitropropyl) Succinate.(1)

We have been studying the chemical reactions of the very reactive explosive intermediate 1,3,5-tribromo-2,4,6-trinitro-benzene in the search for improved high explosives.(2) The chemistry was originally studied in 1888 and then no more work was reported in the literature until recently. Interest was revived in 1,3,5-tribromo-2,4,6-trinitrobenzene in 1948 and again in 1953 in this Laboratory(3). We became most interested in 1,3,5-triamino-2,4,6-trinitrobenzene (TATNB), which was readily prepared from the tribromo compound with alcoholic ammonia. This triamino derivative (TATNB) was found to be quite insensitive to impact, extremely stable to heat, and to have a high crystal density (1.934) and a detonation velocity somewhat superior to TNT at the same percentage of crystal density.

with the revived interest in TATNB, 1,3,5-tris methylamino and 1,3,5-tris methylnitramino-2,4,6-trinitrobenzene were also prepared. The nitramino derivative was sensitive to impact and less stable thermally. Both compounds are new to the chemical literature, but offer no advantage over present service explosives.

One attempt was made to prepare the 1,3,5-tricyano derivative without success. Attempts to react the 1,3,5-tribromo compound with glycine, hydrazine, 5-aminotetrazole, aminoguanidine, and 2,2-dinitropropanel were unsuccessful. Fuerer has reported the successful reaction of glycine with the somewhat similar 1,3-dichloro-2,4,6-trinitrobenzene (4). Hill and Rice of this Laboratory tried unsuccessfully to react trinitroethanol with the similar structure in picryl chloride using aluminum chloride catalysis (5).

EXPERIMENTAL

Preparation of 1,3,5-Triamino-2,4,6-Trinitrobenzene (TATNB).

Absolute alcohol (200 ml.) was saturated with ammonia and then 12.5 g. (0.028 mole) of 1,3,5-tribromo-2,4,6-trinitrobenzene prepared as described in reference 3 was added. The flask was stoppered and allowed to stand at room temperature for a day. Additional ammonia was bubbled into the mixture which was then heated under reflex for thirty minutes, filtered hot, collecting the insoluble product on a Buchner funnel. The product was washed with water, then alcohol, and dried. We recovered 4.7 g. of TATNB. The product was recrystallized from nitrobenzene. Pure TATNB is reported to melt above 360°C. Qualitative analysis for halogen was negative.

Calculated for C6H6N6O6: C, 27.9; H, 2.32; N, 32.55.

Found: C, 28.58, 28.25; H, 2.39, 2.30; N, 31.73, 31.88.

It was found to be almost insoluble in most common solvents which coupled with its high melting point and crystal density probably indicates a high degree of internal hydrogen bonding. The physical properties are given in Table I.

Preparation of 1,3,5-Tris Methylamino-2,4,6-Trinitrobenzene.

Methylamine was bubbled into 100 ml of purified dioxane for ten minutes with stirring, then a solution containing 2.0 g. (0.0042 mole) of 1,3,5-tribromo-2,4,6-trinitrobenzene in 50 ml of benzene was added. A yellow precipitate formed and the reaction mixture started to self heat. The temperature was controlled by gentle cooling with an ice bath. The mixture was stirred for two hours after the addition was completed and then allowed to stand at room temperature for four days. The solid was collected on a Buchner funnel, washed with water and dried. The product was recrystallized from nitromethane. The product melted at 266°C with decomposition. A sodium fusion gave a negative test for halogen.

Calculated for C9H12N6O6: C, 35.95; H, 4.00; N, 28.00.

Found: C, 35.65, 35.69; H, 3.93, 3.69; N, 27.57, 27.22.

The physical properties are given in Table I.

Preparation of 1,3,5-Tris Methylnitromino-2,4,6-Trinitrobenzene.

A 100 ml beaker fitted with a mechanical stirrer and thermometer was charged with 35 ml. of mixed acid of the following composition: 53.4% HNO3, 35.2% 25% oleum, which contained 11.6% free SO3. The acid was cooled to 15°C and 1.0 g. (0.0033 mole) of 1,3,5-tris methylamino-2,4,6-trinitro-benzene added portionwise. The reaction did not self heat or evolves oxides of nitrogen. The mixture was warmed to 50°C over a 40 minute period with agitation, cooled to 5°C and poured on ice. A white precipitate separated immediately and was collected on a sintered glass funnel. The solid was washed with water until acid free and then dried. Recrystallized from an acetone-alcohol mixture, it malted at 193°C. with decomposition. The yield was 15% of theory based on the methylamino starting material.

Calculated for C9H9N9O12: C, 24.8; H, 2.07; N, 28.95.

Found: C, 25.73, 26.25; H, 2.31, 2.33; N, 29.78, 28.94.

The physical properties are tabulated in Table I.

Attempted Preparation of 1,3,5-Tricyano-2,4,6-Trinitrobenzene.

One gram (0.002 mole) of 1,3,5-tribromo-2,4,6-trinitrobenzene dissolved in 50 ml of dry benzene was added to 1.0 g. (0.0112 mole) of cuperous cyanide in 10 ml. of methanol and the mixture refluxed four hours. The color of the mixture turned pale green. The reaction mixture was filtered hot, washed with methanol and evaporated to dryness. The residue was taken up in methanol, treated with charcoal, filtered and chilled at -20°C. A white crystalline solid (0.46 g.) was isolated which sublimed above 240°C. Elemental analysis did not agree with that calculated for the desired reaction product. The solid was not characterized further.

Attempted Preparation of 1,3,5-tris 5-Aminotetrazole-2,4,6-Trinitrobenzene.

A mixture of 1.0 g. (0.002 mole) of 1,3,5-tribromo-2,4,6-trinitrobenzene and 0.7 g. (0.006 mole) of 5-aminotetrazcle in 25 ml. of glacial acetic acid was refluxed six hours and then cooled to room temperature. After standing at room temperature a white solid separated which was isolated and dried, m. 237-44°C. The solid recrystallized from alcohol, melted at 297-8°C. A mixed melting point with an authentic sample of the tribromo compound gave no depression. Under the conditions used we did not obtain any of the desired reaction products.

Attempted Reaction of 1,3,5-Tribromo-2,4,6-Trinitrobenzene with Glycine Ethyl Ester Hydrochloride.

A mixture of 4.0 g. (0.008 mole) of 1,3,5-tribromo-2,4,6-trinitrobenzene, 2.96 g. (0.03 mole) of sodium carbonate and 2.12 g. (0.03 mole) of glycine ethyl ester hydrochloride in 150 ml. of cellosolve was allowed to stand at room temperature for twenty-four hours. The solid separating was water soluble and appeared to be inorganic when heated over an open flame, and aqueous solution on treatment with HCl did not give a precipitate. The filtrate was acidified, diluted with water and chilled. A solid separated which melted at 285°C. Recrystallization from cellosolve recovered a material melting at 294°C and a mixed melting point with an authentic sample of 1,3,5-tribromo-2,4,6-trinitrobenzene gave no depression. Under the conditions tried we were unable to isolate the desired reaction product.

Attempted Preparation of 1,3,5-Trihydrazino-2,4,6-Trinitrobenzene.

A solution of 2.0 g. (0.003 mole) of the tribromotrinitro compound in 40 ml. of cellosolve was warmed at 70°C and a mixture containing 0.8 ml. (0.014 mole) of 85% hydrazine hydrate and 1.4 g. (0.014 mole) of potassium acetate in 15 ml. of cellosolve was added. The reaction mixture turned a deep red color after warming at 60-70°C for one hour, the reaction mixture was filtered to remove the inorganic salt and the filtrate diluted with water and chilled. An oil separated which we were unable to crystallize, or characterize.

Attempted Preparation of 1,3,5-Tris Aminoguanidine-2,4,6-Trinitrobenzene.

A 50% cellosolve solution containing 7.0 g. (0.026 mole) of aminoguanidine sulfate was treated with an aqueous solution of potassium hydroxide (4.4 g., 0.08 mole) and the potassium sulfate filtered off. The aminoguanidine solution was added to a warm solution of 4.0 g. (0.008 mole) of 1,3,5-tribromo-2,4,6-trinitrobenzene in 150 ml. of cellosolve. The reaction mixture was allowed to stand at room temperature of about twenty-four hours. On chilling a solid separated which after recrystallization from ethanol melted at 125°C. Elemental analysis proved the solid was not our desired reaction product. The solid was not characterized further.

Attempted Preparation of 1,3,5-(2,2-dinitropropyl)-2,4,6-Trinitrobenzene.

A mixture of 0.5 g. (0.002 mole) of 1,3,5-triamino-2,4,6-trinitrobenzene and 0.9 g. (0.006 mole) of 2,2-dinitropropanol were suspended in 25 ml. of concentrated sulfuric acid and

the mixture warmed slowly to 100°C, where a solution was complete and deep red in color. The solution was poured on ice and chilled. As a solid did not separate, it was assumed that the desired reaction did not take place under these conditions. At elevated temperature the sulfuric acid probably formed a water soluble salt similar to that formed with aniline in sulfuric acid.

6.0 cc in 2 hrs. 260° C (500°F), at 250° C HMX decomposed in a few minutes. A mixture of the triamino compound with Ba(NO₃) $_2/A$ l @ 250° C gave μ cc in 2 hrs., impact sensitivity was 1μ 3 cm., σ 0.27 with a 2.5 kg. wt.

/B

11.5 cc in 30 minutes @300°C.

থ

TABLE I

	oility Density	2.39	/a,b 1.934		
	y Vacuum Stability cc gas/μ8 hrs. 100°C	N11	0.36/8.0		2,55
PHYSICAL PROPERTIES	Impact Sensitivity	118 cm.	>320 cm.		18 cm.
	m•p•	296 ° C	3 60° C	266°C	. 193°C
	Compound	1,3,5-Tribromo- 2,4,6-trinitro- benzene	1,3,5-Triamino- 2,4,6-trinitro- benzene	1,3,5-tris Methylamino- 2,4,6-trinitro- benzene	l, 3, 5-tris Methyl- nitramino-2, 4, 6- trinitrobenzene

6 CONFIDENTIAL

TABLE II

DETONATION VELOCITY MEASUREMENTS OF 1,3,5-TRIAMINO-2,4,6-TRINITROBENZENE (6)(7)

Density	Velocity (Meters/Sec)
1.290	5380
1.345	5628
1.675	6550
1.675	6575
1.882	7035
1.835	7220 (95% of crystal density)*

* TNT, 6800 m/sec. at 1.57, 95% of crystal density

CONCLUSIONS

TATNE was particularly interesting in its resistance to heat, but it did not appear to offer any other advantages over conventional explosives in present day use. The higher cost of preparation would also rule it out as a substitute for any of the present military high explosives, except for special application. TATNE might prove a useful high explosive for use in the war heads of high speed guided missles or in projectiles carried by jet aircraft where aerodynamic heating is a major problem facing all of the Services today. Present service explosives require elaborate insulation of the warhead and decompose rapidly at temperatures in excess of 200°C (390°F). TATNE appears to be stable for some hours at 260°C (500°F) and such additives as aluminum powder and barium nitrate do not impair this stability. The feasibility of its use in this application is under investigation and the results of the work will be reported at a later date.

The 1,3,5-tris methylamino and 1,3,5-tris methylnitramino-2,4,6-trinitrobenzene do not appear to offer anything useful as new explosives. It is felt that an effort to prepare 1,3,5-tricyano-2,4,6-trinitrobenzene may afford a new and interesting explosive compound, as 2,4,6-trinitrobenzonitrile prepared in this laboratory is known to be a stable compound(8).

We feel that the severe steric hinderance around the bromine atom as well as the tendency toward decomposition in the presence of base obviously limits the scope of the substitution reactions on the tribromo derivative. It is thought that substitution of chlorine for bromine may aid in increasing the scope of the reaction.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the assistance of W. A. Moats and R. L. Beauregard in the synthetic work. The detonation velocity measurements were made by R. H. F. Stresau's group.

LIST OF REFERENCES

- 1. Hill, M. E., NAVORD Report 2965, "Synthesis of New High Explosives". 1 April 1953, Confidential.
- 2. Jackson, C. L., and Wing, J. F., American Chemical Journal 10, 283 (1888).
- 3. Hill, M. E., NAVORD Report 3709, "Large Scale Laboratory Preparation of 1,3,5-Trinitro-2,4,6-Tribromobenzene". 2 February 1953.
- 4. Feuer, H., Research in Polynitro Monomers and Polymers, Quarterly Progress Report No. 2, Cont. NO. N7onr-39411, Project NO. NR230-043, 25 May 1950.
- 5. Hill, M. E., and Rice, R. G., Private Communication on Unpublished data.
- 6. Hampton, L. D., NAVORD Report 3731, "Small Scale Detonation Velocity Measurements from May 1951 to May 1954", June 1954. Confidential.
- 7. Fisher, E. M. and Christian, E. A., NAVORD Report 2986, "Explosion Effects Data Sheets", 14 June 1955, Confidential.
- 8. Kamlet, M. J., NAVORD Report 4398, "2,2-Dinitroethylamine", 22 October 1956, To be published. Confidential.

NAVORD Report Щ05

DISTRIBUTION LIST

	No. o Copie
Chief, Bureau of Ordnance, Washington 25, D. C.	
Attn: Ad-3	1
Attn: ReO6	ī
Attn: ReU3	2
Chief of Naval Research, Washington 25, D. C	2 1
Attn: Code 425	ī
Attn: Code 4.26	ī
Chief of Ordnance, Department of the Army,	-
Washington 25, D. C	1 .
Attn: Research and Development Division	ĩ
Commander, Naval Ordnance Test Station,	_
China Lake, California	2
	2
Commanding Officer, Naval Powder Factory,	1
Indian Head, Maryland	7
Commanding Officer, Naval Mine Depot,	•
Yorktown, Virginia	1
Commanding Officer, Picatinny Arsenal, Dover,	
New Jersey.	_
Attn: Chemistry Research Section	1
Commanding General, Aberdeen Proving Ground, Maryland	
Attn: Ballistics Research Center	1
Commander, Eglin Air Force Base,	
Eglin, Florida.	
Attn: Air Material Test Center	1
Commanding General. Redstone Arsenal	
Huntsville, Alabama	1
Attn: Rohm and Haas Company	1
Director, Naval Research Laboratory,	
Washington 25, D. C	1
Office of Ordnance Research, 2117 Myrtle Drive,	_
Duke University, Durham, North Carolina. Via ONR	'n
	-
Armed Services Technical Information Agency,	
Document Service Center,	مع
Knott Building, Dayton 2, Ohio	5
Solid Propellants Information Agency,	
Applied Physics Laboratory,	
Johns Hopkins University, Silver Spring, Maryland	^
Via: InsOrd	2
George Washington University, Department of Chemistry,	
Washington, D. C.	•
Attn: Prof. W. A. Sager, Via: ONR	1
Los Alamos Scientific Laboratory, P. 0. Box 1663,	
Los Alamos, New Mexico, Via INM	•
Attn: Paports Librarian for Dr. L. C. Smith	1



NAVOTO Report 4405

DISTRIBUTION LIST, (CONT'D)

	No. of Copies
National Northern Corporation, West Hanover, Massachusetts. Attn: Dr. Charles Plummer. Via: InsMat	1.
Via: Director Atomic Energy Commission, San Francisco Operations Office, 1518 17th Street, Oakland, California	1

The second second